

SIMULATION OF THERMOPHYSICAL PROCESSES IN COMPOSITE PRODUCTION BY RTM

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Abstract

A mathematical model describing the behavior of thermosetting matrixes during RTM process was developed using the COMSOL Multiphysics engineering simulation software. The model includes heat generation in the reactor volume due to the partial curing of the resin and heat transfer processes. The heat flow rate of the resin curing was calculated from DSC data using non-isothermal kinetic analysis performed with NETZSCH Thermokinetics 3.0 software. Acceptable operational time was estimated for different resins and temperature conditions to avoid sharp increase of heat release rate in the resin and its precuring.

1 Introduction

Fiber-reinforced composite materials with thermosetting matrixes have a number of significant advantages over traditional materials including high strength-weight ratio, high specific stiffness and good durability.

The Resin Transfer Molding (RTM) is widely used for composite production. Mathematical simulation of this process was carried out in several papers [1-7]. In case of large dimensions and complex shape products manufacture by RTM technique the injection process could proceed for several hours. Therefore a molding material lifetime with a low viscosity at elevated temperatures is one of the key process parameters. Usually the molding material is preheated and then is injected from the reactor to mold cavities. It is often rather difficult or impossible to experimentally establish the molding material lifetime for a specific technological process and equipment. Therefore, the aim of this work was to develop a mathematical model describing the behavior of thermosetting resins, and the calculation of the time limit before the explosive exothermic process starts in the given technological conditions. The model was developed for the reactor with heated walls and bottom while stirring with a mixer installed in the lid of the reactor.

The model includes heat generation in the reactor volume due to the partial curing of the resin and heat transfer processes. The model was developed using the COMSOL Multiphysics engineering simulation software [8]. The problem was solved by finite element method. The

heat flow rate of the resin curing for a given temperature program was calculated using non-isothermal kinetic analysis performed with NETZSCH Thermokinetics 3.0 software [9]. Kinetic analysis was made using the differential scanning calorimetry (DSC) data.

2 Materials and testing methods

Two thermoset resins were investigated. Resin R1 [10] was a mixture of tetraglycidylmethylenedianiline (TGDDM) and two aromatic amines. Analysis of DSC data (Fig. 1), Arrhenius parameters of kinetic models (Tables 1, 2), and rheological studies data (Fig. 3) has shown a relatively high reactivity of the resin R1. In order to reduce the reactivity we developed our resin E1 with another type of curing agent – chlorinated amine curing agent. Chlorine atoms in the structure of the amine led to a significantly lower activity of curing agent and slowed down the curing rate. Hence E1 resin curing proceeds slower than R1 resin curing. It leads to different acceptable conditions for the resin preparation before infusion to the molding form. We expect that the use of chlorinated amine curing agent increases the acceptable working time for reactor with E1 resin.

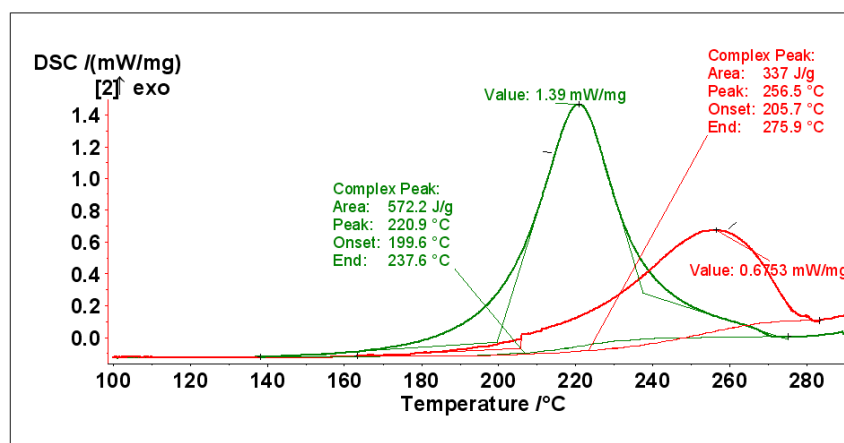


Figure 1. Comparison of DSC curves of the curing process for R1 resin (green curve) and E1 resin (red curve).

DSC measurements were carried out using DSC 204 Phoenix calorimeter (NETZSCH Geratebau GmbH). The specimens were heated in the instrument with the heating rates of 1, 2.5, 5, 10 and 20 K/min in the temperature range of 30-320 °C in dry air or argon atmosphere with a constant flow of 100 ml/min.

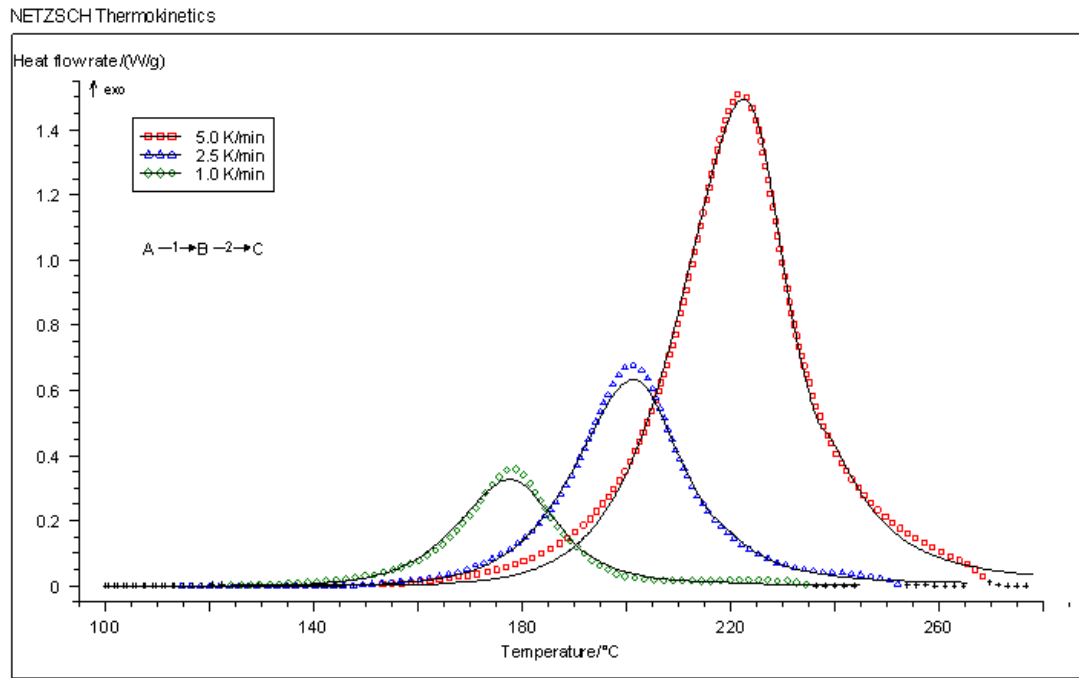


Figure 2. Approximation of R1 curing DSC curves with a two-step model.

DSC curves were used to calculate kinetic parameters of curing process. The software [9] was described by Opfermann [11] and was successfully used earlier [12]. Model-free methods and model-fitting methods were implemented in the software. Model-free methods were used to calculate Arrhenius parameters of process such as apparent activation energy E_a/R and pre-exponential factor A (Eq. 1). The parameters were estimated using Ozawa–Flynn–Wall [13] isoconversional method. The obtained values were used as initial values for non-regression procedure.

$$\frac{d\alpha}{dT} = A \cdot e^{\left(\frac{-E_a}{RT}\right)} \cdot f(\alpha) \quad (1)$$

where A is pre-exponential factor, E_a/R is apparent activation energy, $f(\alpha)$ – conversional function corresponding to process mechanism, α – degree of conversion. Statistical analysis allows to choose $f(\alpha)$ function with minimal sum of least squares of deviations between calculated DSC curves and experimental ones. We revealed that the best approximation of the R1 resin curing DSC curves was obtained using the two-step model of consecutive reactions with autocatalysis (Eq. 2, Fig. 2). Kinetic parameters are shown in Table 1. DSC curves for E1 curing were approximated with one-step model (Eq. 3, Table 2).

$$f(\alpha) = (1 - \alpha)^n \cdot \alpha^a \quad (2)$$

$$f(\alpha) = (1 - \alpha)^n \cdot (1 + KcatX) \quad (3)$$

Rheological analysis was carried out with Brookfield CAP 2000+H Viscometer. Changes in the resin viscosity during heating and isothermal treatment were measured (Fig. 3).

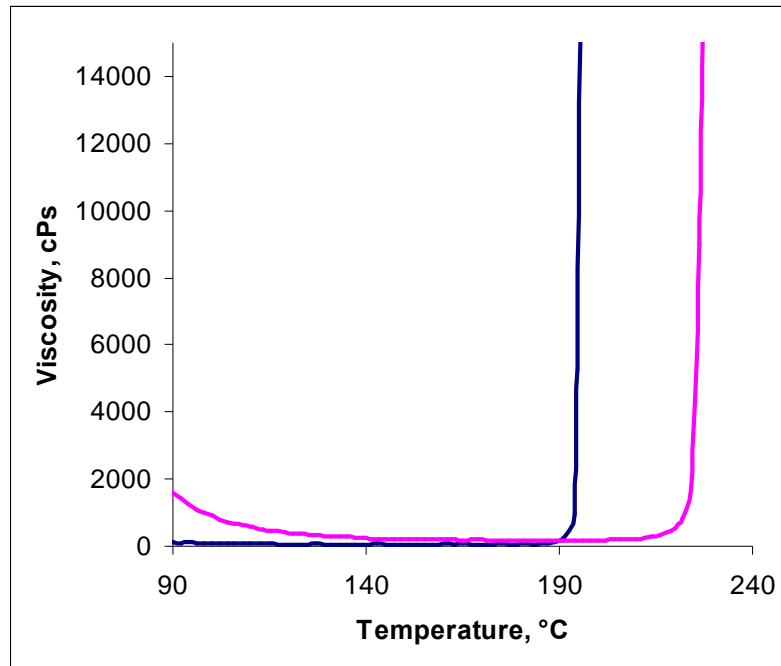


Figure 3. R1 resin viscosity (blue curve) and E1 resin viscosity (magenta curve).

Experimental measurement of thermal conductivity and heat capacity of the resin samples was carried out with NETZSCH LFA 457 MicroFlashTM instrument by pulse method (laser flash method) according to ASTM E-1461, DIN EN 821 or DIN 30905 standards.

The operational mode should be optimized to avoid sharp increase of heat release rate in the resin and to avoid rapid increase of resin temperature and its precuring. On the basis of the developed mathematical model acceptable operational time for the reactor was defined before the rapid resin curing starts. Acceptable operational time was estimated as a period when the reactor was locally heated to 210 °C temperature. This leads to sharp increase in curing rate and heat release rate. Acceptable operational times were defined for both R1 and E1 resins at different temperature conditions in the reactor. We showed that the less reactive E1 resin can be stored even in fully loaded reactor for 15 hours at 140 °C and for 24 hours at 100 °C. More reactive R1 resin can be stored in a fully loaded reactor for no more than 7-8 hours at temperatures of 100-140°C. Acceptable operational time can be increased by reducing the load of the reactor due to reducing of resin self-heating.

Parameter	Value
First step (first peak)	
Log A_1 , s^{-1}	4.31
E_1 , kJ/mol	60.21
Reaction order n_1	0.64
Parameter a_1	0.69
Second step (second peak)	
Log A_2 , s^{-1}	3.76
E_2 , kJ/mol	53.66
Reaction order n_2 ,	2.2
Parameter a_2	0.69
Foll. React.	0.76

Table 1. Kinetic parameters of R1 resin curing.

Parameter	Value
First step (first peak)	
Log A_1 , s ⁻¹	4.31
E_1 , kJ/mol	60.21
Reaction order n_1	0.64
Parameter a_1	0.69
Second step (second peak)	
Log A_2 , s ⁻¹	3.76
E_2 , kJ/mol	53.66
Reaction order n_2 ,	2.2
Parameter a_2	0.69
Foll. React.	0.76

Table 2. Kinetic parameters of R1 resin curing.

Conclusions

A mathematical model describing the behavior of thermosetting matrixes during RTM process was developed. Acceptable operational time was estimated for different matrixes and temperature conditions to avoid sharp increase of heat release rate in the resin and its precuring. The developed mathematical model can be used for the optimization and operational mode selection depending on the type of curing agent, resin lifetime and maximum reactor loading.

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